

Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

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Introduction

While ASME and API design codes and standards provide rules for the design, fabrication, inspection, and testing of new pressure vessels, piping systems, and storage tanks, they do not address equipment deterioration while in service, nor do they account for original fabrication defects not discovered during construction but found during subsequent inspections.

The interactions between the materials of construction and the environmental conditions to which they are exposed, including process conditions and external conditions, are extremely varied within an operating oil refinery. Oil refineries contain many different processing units, each having its own combination of process streams and temperature/pressure conditions. The purpose of this recommended practice is to describe the wide variety of service-induced damage and deterioration mechanisms, including corrosion and other types of metallurgical damage, that are most likely to affect the condition of the materials of construction commonly used in refinery equipment.

This document incorporates information gathered from major incidents in the refining industry and is intended to be consistent with applicable API documents as well as other related industry standards and practices. It is meant to provide guidance to pressure equipment integrity personnel but should not be considered the final technical basis for damage mechanism assessment and analysis or inspection and monitoring. The damage mechanism descriptions herein are not intended to provide a definitive guideline for every possible situation that may be encountered, and the reader may need to consult with an engineer or other corrosion specialist familiar with applicable degradation modes and failure mechanisms, particularly those that apply in special cases.

Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

1 Scope

This recommended practice discusses damage mechanisms applicable to oil refineries; however, much of the information herein can also be applied to petrochemical and other industrial applications, as the user deems appropriate. It is up to the user to determine the applicability and appropriateness of the information contained herein as it applies to their facility.

API 571 is a reference document that provides useful information by itself and also complements other API standards and recommended practices. The document should be utilized as a reference to other integrity related documents. It is intended to contribute to the overall management of pressure equipment integrity and is a useful resource for many mechanical integrity program activities including:

- a) identification of existing damage or deterioration and anticipated rates of degradation,
- b) identification of future damage mechanism susceptibilities,
- c) development and maintenance of inspection and monitoring strategies, programs, and plans (e.g. per API 510, API 570, and API 653),
- d) implementation and monitoring of integrity operating windows (IOWs) (see API 584),
- e) development of corrosion control documents (CCDs) (see API 970),
- f) implementation of Risk-Based Inspection (RBI) programs (see API 580 and API 581),
- g) conducting Fitness-For-Service (FFS) assessments (see API 579-1/ASME FFS-1),
- h) application of proper examination techniques, and
- i) conducting pressure equipment integrity incident investigations (see API 585).

The information for each damage mechanism is provided in a set format as shown below.

- **Name of the Mechanism**—The term commonly used to describe or name the mechanism.
- **Description of Damage**—A basic description of the damage mechanism.
- **Affected Materials**—A list of the materials prone to the damage mechanism.
- **Critical Factors**—A list of factors that affect the damage mechanism (i.e. rate of damage).
- **Affected Units or Equipment**—A list of the affected equipment and/or units where the damage mechanism commonly occurs. This information is also shown on generic process flow diagrams (PFDs) for typical process units.
- **Appearance or Morphology of Damage**—A description of the damage mechanism, with pictures in some cases, to assist with recognition of the damage.
- **Prevention/Mitigation**—Methods to prevent or mitigate the damage and in some cases to evaluate by engineering analysis.

- **Inspection and Monitoring**—Guidance for nondestructive examination (NDE) and other methods for detecting, monitoring, characterizing, sizing, and determining the severity or extent of damage or deterioration.
- **Related Mechanisms**—A list of related damage mechanisms.
- **References**—A list of references cited, relied upon, or that provide background and other pertinent information.

Generic PFDs are provided in [Section 4](#) to assist the user in determining primary locations where some of the significant damage mechanisms are commonly found.

2 Terms and Definitions

2.1 Definitions

For the purposes of this document, the following definitions apply.

2.1.1

austenitic

A term that refers to a type of metallurgical structure (austenite) normally found in 300 series stainless steel (SS) and nickel-based alloys. These materials have a face centered cubic crystallographic structure and are generally nonmagnetic.

2.1.2

austenitic stainless steels

The 300 series SS, which commonly include Types 304, 304L, 304H, 309, 310, 316, 316L, 316H, 317, 317L, 321, 321H, 347, and 347H. The “L” and “H” suffixes refer to controlled ranges of low and high carbon content, respectively. These alloys are characterized by an austenitic structure.

2.1.3

carbon steel

An alloy consisting primarily of iron (Fe) with a small amount of carbon (C). Carbon steels do not have alloying elements intentionally added. However, there may be small amounts of elements permitted by specifications such as ASTM A516 and ASTM A106, for example, that can affect corrosion-related properties, hardness after welding, and toughness. Elements that may be found in small quantities include Mn, Cr, Ni, Mo, Cu, S, Si, P, Al, V, and B.

2.1.4

diethanolamine

DEA

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.5

diglycolamine

DGA

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.6

duplex stainless steel

A family of stainless steels that contain a mixed austenitic-ferritic structure including Alloys 2205, 2304, and 2507. The welds of 300 series SS may also exhibit a duplex structure.

2.1.7**ferritic**

A term that refers to a type of metallurgical structure (ferrite) normally found in carbon and low-alloy steels and many 400 series SS. These materials have a body centered cubic crystallographic structure and are generally magnetic.

2.1.8**ferritic stainless steels**

A family of stainless steels including Types 405, 409, 410S, 430, 442, and 446.

2.1.9**heat-affected zone****HAZ**

The portion of the base metal adjacent to a weld that has not been melted, but in which the metallurgical microstructure and mechanical properties have been changed by the heat of welding, sometimes with undesirable effects.

2.1.10**high-strength low-alloy steel****HSLA steel**

A family of carbon steels in which higher strength levels are achieved by the addition of moderate amounts of alloying elements such as titanium, vanadium, or niobium in amounts of less than 0.1 %. They can be more sensitive to cracking during fabrication from hydrogen embrittlement (HE) (delayed cracking; also known as underbead cracking).

2.1.11**low-alloy steel**

A family of steels containing up to 9 % chromium and other alloying additions for high temperature strength and creep resistance. The low-alloy steels commonly encountered in refining include C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1.0Mo, 5Cr-0.5Mo, and 9Cr-1Mo. These are considered ferritic steels, although their microstructures might be an alteration of the ferrite phase found in carbon steel.

2.1.12**martensitic**

A term that refers to a type of hard metallurgical structure (martensite) normally found in some 400 series SS. Heat treatment or welding followed by rapid cooling can sometimes produce this or a similar hard metallurgical structure in carbon and low-alloy steels. Martensitic and similar hard microstructures typically need to be tempered by heat treatment to soften them in order to make the material suitable for use in refining applications.

2.1.13**martensitic stainless steel**

A family of stainless steels including Types 410, 416, 420, 440A, 440B, and 440C.

2.1.14**methyl diethanolamine****MDEA**

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.15**monoethanolamine****MEA**

Chemical used in amine treating to remove H₂S and CO₂ from hydrocarbon streams.

2.1.16**nickel-based**

A family of alloys containing nickel as a major alloying element (>30 % Ni) including Alloys 200, 400, K-500, 800, 800H, 825, 600, 600H, 617, 625, 718, X-750, and C276.

2.1.17**stainless steel**

An alloy of iron (Fe) with at least 10.5 % chromium (Cr) plus other alloy additions, depending on the specific grade. There are four major categories of stainless steels that are characterized by their metallurgical structure at room temperature: austenitic, ferritic, martensitic, and duplex. These alloys have varying amounts of chromium and other alloying elements that give them resistance to certain types of degradation depending on the alloy.

2.2 Acronyms and Abbreviations

For the purposes of this document, the following acronyms and abbreviations apply.

ABSA	angle beam spectral analysis
ACFM	alternating current field measurement
ACSCC	alkaline carbonate stress corrosion cracking
AET	acoustic emission testing
AGO	atmospheric gas oil
Al	aluminum
ARH	acid relief header
ARN	acid relief neutralizer
ASCC	alkaline stress corrosion cracking
AUBT	automated ultrasonic backscatter testing
AUT	automated ultrasonic testing
B	boron
BFW	boiler feedwater
C	carbon
C3	chemical symbol referring to propane or propylene
C4	chemical symbol referring to butane or butylene
Cat	catalyst or catalytic
CCR	continuous catalytic reforming
CH ₄	methane
Cl ⁻ SCC	chloride stress corrosion cracking
CO	carbon monoxide
CO ₂	carbon dioxide

Cr	chromium
Cu	copper
CuF	cuprous fluoride
CuF ₂	cupric fluoride
CUI	corrosion under insulation
CVN	Charpy V-notch
CW	cooling water
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropylamine
DMW	dissimilar metal weld
DNB	departure from nucleate boiling
ECT	eddy current testing
EMAT	electromagnetic acoustic transducer
FAC	flow accelerated corrosion (in boiler water and steam condensate)
FCC	fluid catalytic cracker
Fe	iron
Fe ₃ O ₄	magnetite
FeS	iron sulfide
FFS	Fitness-For-Service
FGE	fuel grade ethanol
FMR	field metallographic replication
FRP	fiber-reinforced plastic
GWT	guided wave testing
H ₂	diatomic hydrogen gas
HAZ	heat-affected zone
HB	Brinell hardness number
HCGO	heavy coker gas oil
HCl	hydrochloric (acid)
HCN	hydrogen cyanide
H ₂ CO ₃	carbonic acid

HE	hydrogen embrittlement
HF	hydrofluoric (acid)
Hg	mercury
HHPS	hot high-pressure separator
HIC	hydrogen-induced cracking
HP	high pressure
HPS	high-pressure separator
HRC	Rockwell hardness number (based on Rockwell C scale)
HRSG	heat-recovery steam generator
H ₂ S	hydrogen sulfide
HSAS	heat stable amine salts
HSLA	high-strength low-alloy
H ₂ SO ₄	sulfuric acid
HCO	heavy cycle oil
HTHA	high-temperature hydrogen attack
HVGO	heavy vacuum gas oil
ID	inside diameter
IOW	integrity operating window
IRIS	internal rotating inspection system
K.O. or KO	knock out, as in K.O. drum
KOH	potassium hydroxide
LCGO	light coker gas oil
LCO	light cycle oil
LP	low pressure
LPS	low-pressure separator
LVGO	light vacuum gas oil
MAWP	maximum allowable working pressure
MDEA	methyl diethanolamine
MDMT	minimum design metal temperature
MEA	monoethanolamine
MFL	magnetic flux leakage

MIC	microbiologically influenced corrosion
Mn	manganese
Mo	molybdenum
MPT	minimum pressurization temperature
mpy	mils per year
MT	magnetic particle testing
MVP	materials verification program
Na	sodium
NAC	naphthenic acid corrosion
NaOH	sodium hydroxide
Nb	niobium
NDE	nondestructive examination
NFT	near-field testing
NH ₃	ammonia
NH ₄ HS	ammonium bisulfide
Ni	nickel
NO ₂	nitrogen dioxide
NPSH	net positive suction head
O ₂	oxygen
OD	outside diameter
P	phosphorus
PAUT	phased array ultrasonic testing
PEC	pulsed eddy current
PFD	process flow diagram
PMI	positive materials identification
POX	partial oxidation
PREN	pitting resistance equivalent number
PT	liquid penetrant testing
PTA SCC	polythionic acid stress corrosion cracking
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride

PWHT	postweld heat treatment
RE	residual element
RFT	remote field testing
RT	radiographic testing
S	sulfur
SAW	submerged-arc welding
SCC	stress corrosion cracking
SEM	scanning electron microscope
Si	silicon
SLOFEC	saturated low-frequency eddy current
SO ₂	sulfur dioxide
SOHIC	stress-oriented hydrogen-induced cracking
SRB	sulfate-reducing bacteria
SRC	stress relaxation cracking
SRU	sulfur recovery unit
SS	stainless steel
SSC	sulfide stress cracking
SW	sour water
SWS	sour water stripper
SWUT	shear wave ultrasonic testing
TAN	total acid number
Ti	titanium
TOFD	time of flight diffraction
UT	ultrasonic testing
UTS	ultimate tensile strength
V	vanadium
VT	visual inspection (visual testing)
WFMT	wet fluorescent magnetic particle testing
Zn	zinc

3 Damage Mechanisms

This section describes the damage mechanisms found in refinery equipment. It includes low- and elevated-temperature corrosion, metallurgical and mechanical damage, environment-assisted cracking, and a few mechanisms that do not necessarily fit into any of these categories.

Section 4 contains PFDs for process units commonly found in refining. These PFDs show the location in the unit where specific damage mechanisms are most likely to be found.

3.1 885 °F (475 °C) Embrittlement

3.1.1 Description of Damage

885 °F (475 °C) embrittlement is a loss of ductility and fracture toughness due to a metallurgical change that can occur in stainless steels containing a ferrite phase as the result of exposure in the temperature range 600 °F to 1000 °F (315 °C to 540 °C). The embrittlement can lead to cracking failure.

3.1.2 Affected Materials

- a) 400 series SS (e.g. 405, 409, 410, 410S, 430, and 446).
- b) Duplex stainless steels such as Alloys 2205, 2304, and 2507.
- c) Austenitic (300 series) stainless steel weld metals, which normally contain up to about 10 % ferrite phase to prevent hot cracking during welding.

3.1.3 Critical Factors

- a) The alloy composition, particularly chromium content, amount of ferrite phase, and operating temperature are critical factors.
- b) The lower-chromium alloys (e.g. 405, 409, 410, and 410S) are less susceptible to embrittlement. The higher chromium ferritic stainless steels [e.g. 430 (16 % to 18 % Cr) and 446 (23 % to 27 % Cr)] and duplex stainless steels (22 % to 25 % Cr) are much more susceptible.
 - 1. Although it has not yet been shown in all 300 series SS weld metals, Charpy impact testing of Type 308 and Type 347H SS weld metal aged in approximately the 850 °F to 885 °F (455 °C to 475 °C) temperature range has found evidence of 885 °F (475 °C) embrittlement, with individual sample results in some cases being less than 15 ft-lb (20 J) at ambient temperatures. However, 885 °F (475 °C) embrittlement of austenitic stainless steel weld metal historically has not been found to be a significant concern in typical refining applications.
- c) Increasing amounts of ferrite phase in duplex stainless steels increase susceptibility to damage when operating in the high-temperature range of concern. A dramatic increase in the ductile-to-brittle transition temperature will occur. Duplex stainless steels also need to be cooled rapidly after welding to avoid formation of embrittling phases.
- d) High-temperature exposure is required for embrittlement. A primary consideration is operating time at temperature within the critical temperature range. Damage is cumulative and results from the formation of an embrittling ordered metallic phase (alpha prime phase) that occurs most readily at approximately 885 °F (475 °C). Additional time is required to reach maximum embrittlement at temperatures above or below 885 °F (475 °C). For example, many thousands of hours may be required to cause embrittlement at 600 °F (315 °C).
- e) As a practical matter, since equipment is typically in service for years, it is often assumed that susceptible materials that have been exposed to temperatures in the 600 °F to 1000 °F (370 °C to 540 °C) range are affected.
- f) The effect on toughness is not pronounced at the operating temperature but is significant at lower temperatures experienced during plant shutdowns, start-ups, or upsets.

- g) Embrittlement can also result from heat treatment if the material is held within or cooled slowly through the embrittlement range.

3.1.4 Affected Units or Equipment

- a) 885 °F (475 °C) embrittlement can be found in any unit where susceptible alloys are exposed to the embrittling temperature range.
- b) Most refining companies limit the use of ferritic stainless steels to non-pressure-boundary applications because of this damage mechanism.
- c) Common examples include fractionator trays and internals in high-temperature vessels used in crude, vacuum, fluid catalytic cracker (FCC), and coker units. Typical failures include cracking when attempting to weld or to straighten bent, upset tower trays made of Type 409 and 410 SS. (This occurs often with vacuum tower trays of this material.)
- d) Other examples include duplex stainless steel heat exchanger tubes and other components exposed to temperatures above 600 °F (315 °C) for extended time periods. Duplex stainless steels are normally limited to a maximum service temperature of 600 °F (315 °C).

3.1.5 Appearance or Morphology of Damage

- a) 885 °F (475 °C) embrittlement is a metallurgical change that is not readily apparent with metallography.
- b) The existence of 885 °F (475 °C) embrittlement can possibly be identified by an increase in hardness in affected areas. Failure during bend testing or impact testing of samples removed from service is the most positive indicator of 885 °F (475 °C) embrittlement. ([Figure 3-1-1](#))
- c) Most cases of embrittlement are found in the form of cracking during turnarounds or during start-up or shutdown when the material is at lower temperature where the effects of embrittlement are most detrimental. Embrittled 410 SS has been shown to require a temperature of about 350 °F (175 °C) before adequate toughness has been restored.

3.1.6 Prevention/Mitigation

- a) The best way to prevent 885 °F (475 °C) embrittlement is to avoid exposing the susceptible material to the embrittling range or to use a non-susceptible material. In some cases, users accept the possibility of embrittlement of non-pressure-containing components, e.g. trays and other internals, and deal with the possibility or consequences during maintenance.
- b) Cracking of embrittled material can often be avoided through temperature controls during start-up and shutdown.
- c) It is possible to minimize the effects of embrittlement through modifications in the chemical composition of the alloy; however, resistant material may not always be readily available in most commercial forms.
- d) 885 °F (475 °C) embrittlement is reversible by heat treatment followed by rapid cooling. The de-embrittling heat treatment temperature is typically 1100 °F (595 °C) or higher and may not be practical for many equipment items. If the de-embrittled component is exposed to the same service conditions, it will re-embrittle faster than it did initially.

3.1.7 Inspection and Monitoring

This damage mechanism is very difficult to find prior to equipment failure. It is also time dependent and may take a while to develop in service. Online inspection is not applicable. Awareness of susceptible equipment can help direct inspection planning.

- a) The most effective method of detecting or confirming 885 °F (475 °C) embrittlement is removing and impact or bend testing a sample of the suspect material. Failure during a simple bend test is the most common

method of confirming 885 °F (475 °C) embrittlement in thin components like tower trays. Metallographic examination is typically not effective because the embrittlement-causing phase in the microstructure is so difficult to find or see.

- b) Cracking may be visually apparent in certain types of trays and other non-pressure-containing hardware that have cracked during maintenance or repair activities.
- c) Field hardness testing may distinguish embrittled from non-embrittled material, but hardness testing alone is generally not definitive. Also, the hardness test itself may produce cracking, depending on the degree of embrittlement.
- d) Hammer testing (“field impact testing”) is considered a destructive test. Tapping a suspect component with a hammer may crack the component, depending on the degree of embrittlement. Hammer testing might confirm that a component is not badly embrittled, if it does not crack, or that it is embrittled, if it does crack.

3.1.8 Related Mechanisms

Sigma phase embrittlement (3.56).

3.1.9 References

1. *High-temperature Characteristics of Stainless Steels, Designers' Handbook Series*, American Iron and Steel Institute, Washington, DC, 1979.
2. G.E. Moller, “Experiences with 885 °F (475 °C) Embrittlement in Ferritic Stainless Steels,” *Materials Protection*, NACE International, May 1966.
3. S.A. David, J.M. Vitek, and D.J. Alexander, “Embrittlement of Austenitic Stainless Steel Welds,” Office of Scientific and Technical Information Technical Reports, (University of North Texas Libraries Government Documents Department, <https://digital.library.unt.edu/ark:/67531/metadc741815/>), June 1995.

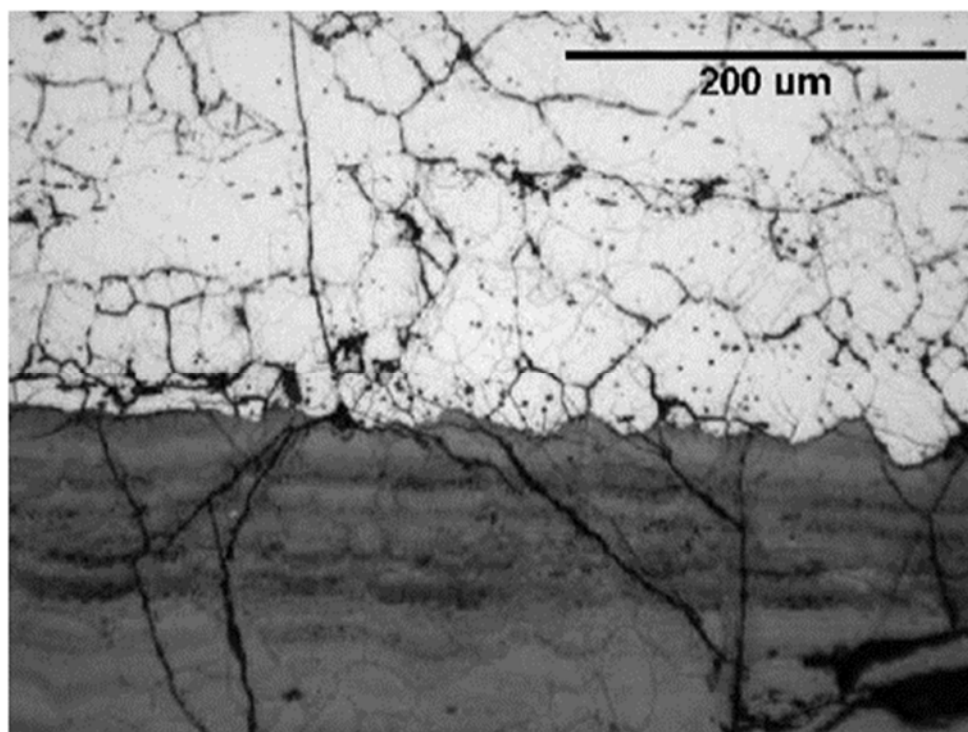


Figure 3-1-1—Sample of cracked material with intergranular cracks visible in the microstructure, suggesting severe embrittlement.

3.2 Amine Corrosion

3.2.1 Description of Damage

- a) Amine corrosion is typically localized corrosion that occurs principally on carbon steel in amine treating processes. Corrosion is not caused by the amine itself but results from dissolved acid gases (CO_2 and H_2S), heat stable amine salts (HSAS), amine degradation products (e.g. bicine, oxalate, and formate salts), and other contaminants.
- b) SCC of carbon steel in amine services is discussed in [3.3](#).

3.2.2 Affected Materials

Primarily carbon steel. 300 series SS and other grades of stainless steel are more resistant.

3.2.3 Critical Factors

- a) Corrosion depends on design and operating practices, the type of amine, contaminants, temperature, and velocity.
- b) Amine corrosion is very closely tied to the operation of the unit. With a few exceptions, carbon steel is suitable for most components in a properly designed and operated unit. Most problems can be traced to faulty design, poor operating practices, or solution contamination.
- c) Corrosion is also dependent on the type of amine used. In general, alkanolamine systems can be rated in order of aggressiveness from most to least as follows: monoethanolamine (MEA), diglycolamine (DGA), diisopropylamine (DIPA), diethanolamine (DEA), and methyl diethanolamine (MDEA).
- d) Lean amine solutions are generally not corrosive because they have low conductivity and high pH. However, an excessive accumulation of heat stable salts, e.g. bicine, oxalate, formate, and acetate salts above about 2 %, depending on the amine, can significantly increase corrosion rates in hot lean amine.
- e) Oxygen in-leakage causes high corrosion rates and contributes to heat stable salt formation.
- f) Lean amine solutions contain a small amount of H_2S , which helps maintain a stable iron sulfide film. Overstripped lean amine solutions can be corrosive if there is inadequate H_2S present to maintain the protective iron sulfide film.
- g) Corrosion rates increase with increasing temperature, particularly in rich amine service. Temperatures above about 220 °F (105 °C) can result in acid gas flashing, if the pressure drop is high enough, with severe localized corrosion.
- h) Process stream velocity will influence the amine corrosion rate and nature of attack. Corrosion is generally uniform; however, high velocities and turbulence will cause localized thickness losses. For carbon steel, velocities are generally limited to 3 fps to 6 fps (1 m/s to 2 m/s) for rich amine and about 20 fps (6 m/s) for lean amine.

3.2.4 Affected Units or Equipment

- a) Amine units, which remove H_2S , CO_2 , and mercaptans from process streams in many units including crude, coker, FCC, hydrogen-reforming, hydroprocessing, and tail gas units.
- b) The regenerator reboiler, including the feed and return lines, and the regenerator are areas where the temperature and turbulence are the highest in the amine system and therefore are locations of potentially significant corrosion.
 - 1. If excessive regeneration occurs in the reboiler (i.e. > 5 % of the total amine regeneration occurs in the reboiler), it can lead to acid gas corrosion in the reboiler, its vapor return line, and the bottom of the regenerator.

2. Ammonia, H_2S , and hydrogen cyanide (HCN) accelerate corrosion in the regenerator overhead condenser and outlet piping as well as reflux piping, valves, and pumps.
- c) The rich amine side of the lean/rich exchangers, the hot lean amine piping, the hot rich amine piping, the stripper overhead condenser piping, the amine solution pumps, and the reclaimers are also areas where corrosion problems commonly occur.
- d) In amine absorber systems, the locations most susceptible to amine corrosion are where amine or acid gas impinge on the shell, as well as downstream of pressure letdown valves and other areas of high velocity in the rich amine piping.

3.2.5 Appearance or Morphology of Damage

- a) Carbon steel and low-alloy steels mostly suffer uniform thinning in localized (isolated) locations or localized under-deposit attack. (Figure 3-2-1 to Figure 3-2-6)
- b) When the process stream velocity is low, thinning will be more uniform and widespread. At locations with high velocity or turbulence, it will be more localized with greater metal loss.
- c) Welds can be preferentially attacked. (Figure 3-2-1 and Figure 3-2-3)

3.2.6 Prevention/Mitigation

- a) Proper operation to the amine system is the most effective way to control corrosion, with particular attention paid to acid gas loading levels. In addition, to avoid corrosive amine degradation products, the process temperature should not exceed recommended limits. Proper control of the reboiler rate and temperature is necessary in order to maintain proper regenerator temperatures.
- b) Proper attention should be given to avoiding the buildup of heat stable salts to unacceptable levels.
- c) The system design should incorporate measures to control local pressure drop to minimize flashing. In areas where it is unavoidable, upgrading to 300 series SS or other corrosion-resistant alloys may be needed. Type 410 SS trays and internals are commonly used in absorber and stripping towers.
- d) Avoid air ingress into the system as this will lead to formation of corrosive heat stable salts.
- e) Storage tanks and surge vessels should be blanketed with oxygen-free inert gas to prevent introduction of oxygen and in-leakage of air.
- f) Solids and hydrocarbons should be removed from the amine solution by filtration and through process control.
- g) Corrosion inhibitors may be required to control amine corrosion within acceptable levels.

3.2.7 Inspection and Monitoring

- a) Visual inspection (VT) of internal surfaces at flow impingement areas, turbulent flow areas, liquid/vapor interfaces, and of welds/heat-affected zones (HAZs) is effective in identifying localized corrosion. Sometimes a pit gauge is used in conjunction with visual examination to provide specific data on extent of metal loss.
- b) Thin regions:
 1. external ultrasonic testing (UT) is typically used to map the thickness of components to identify local thin regions;
 2. profile radiographic testing (RT) can be effective for identifying localized attack, particularly at welds/HAZs and turbulent locations;

3. UT can sometimes be used in conjunction with VT, laser scanning, structured white light imaging, and/or pit gauges to determine the extent of metal loss.
- c) Permanently mounted thickness monitoring sensors can be used.
- d) Corrosion monitoring can be performed by installing corrosion coupons and/or inserting corrosion probes.
- e) The level of amine degradation products (e.g. bicine, oxalate, and formate salts), should be monitored. An increase in iron content of the amine solution will coincide with an increase in the level of these degradation products.
- f) Fouling of exchangers and filters can be a sign of corrosion problems on the unit.

3.2.8 Related Mechanisms

Amine SCC (3.3).

3.2.9 References

1. J. Gutzeit, "Refinery Corrosion Overview," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 171–189.
2. L.R. White and D.E. Street, "Corrosion Control in Amine Treating Units," *Proceedings of the Special Symposium on Corrosion in the Oil Refining Industry*, NACE International, Houston, TX, 1996.
3. R.B. Nielsen et al., "Corrosion in Refinery Amine Systems," Paper No. 571, *Corrosion/95*, NACE International, Houston, TX.
4. API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*, American Petroleum Institute, Washington, DC.
5. M.A. Saleem and A.A. Hulaibi, "Corrosion Challenges in Gas Treating Units," Paper No. 08416, *Corrosion/2008*, NACE International, Houston, TX.
6. P. Quiroga et al., "Improving Amine Unit Reliability with On-line Corrosion Monitoring & Modeling," Paper No. 08421, *Corrosion/2008*, NACE International, Houston, TX.
7. D. Fan et al., "Role of Impurities and H₂S in Refinery Lean DEA System Corrosion," Paper No. 00495, *Corrosion/2004*, NACE International, Houston, TX.



Figure 3-2-1—Localized amine corrosion at the weld found in piping from the reboiler to the regenerator tower in an MEA unit. Many other similar cases were found, some going as deep as half thickness. They were originally found with shear wave UT inspection and mistaken as cracks.



Figure 3-2-2—Hot lean amine corrosion of carbon steel attributed to increased CO₂ content in the MEA solution.



Figure 3-2-3—Preferential weld corrosion in lean amine. (Reference 5)



Figure 3-2-4—Preferential corrosion in an amine regenerator reboiler return elbow. (Reference 6)

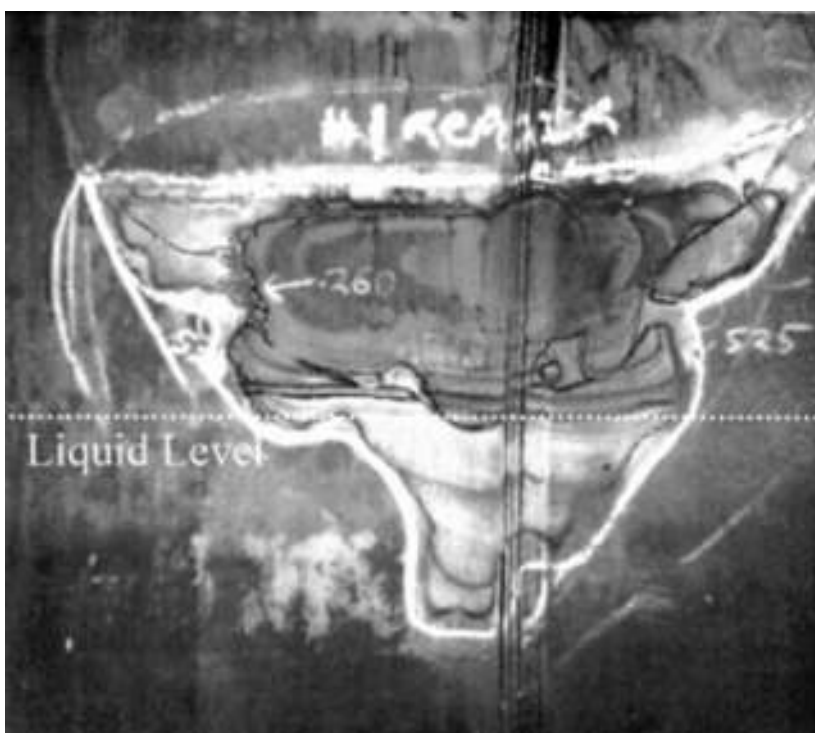


Figure 3-2-5—Corrosion near the liquid level in a reboiler exchanger shell from an amine regeneration unit. (Numbers drawn on figure are UT thicknesses in inches.)
Nominal wall: 0.550 in. (Reference 7)

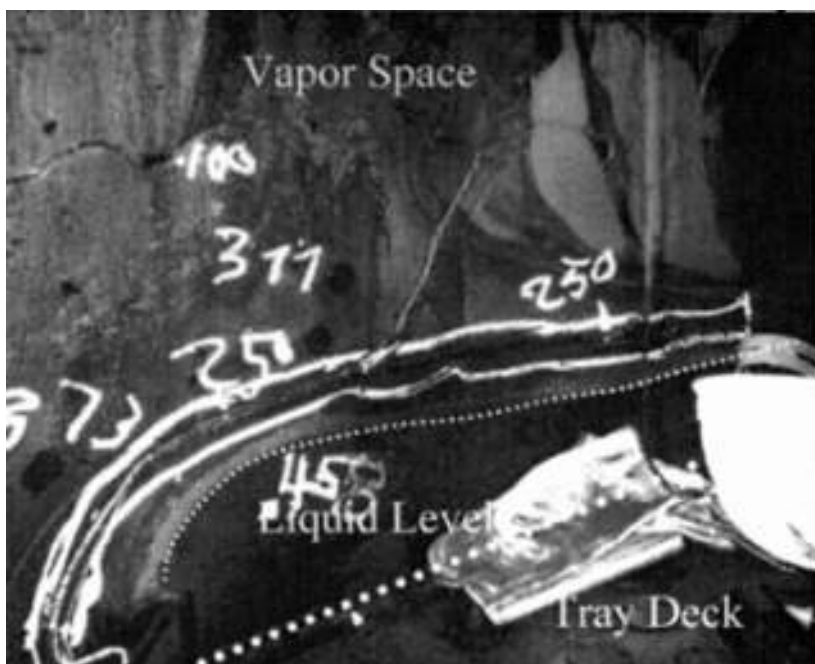


Figure 3-2-6—Corroded amine regenerator column shell near a downcomer. (Numbers drawn on figure are UT thicknesses in inches.) Nominal wall: 0.5 in. (Reference 7)

3.3 Amine Stress Corrosion Cracking

3.3.1 Description of Damage

- a) Amine SCC (or amine cracking) is the cracking of steels under the combined action of tensile stress and an aqueous alkanolamine solution used to remove (absorb) H_2S and/or CO_2 and their mixtures from various gas and liquid hydrocarbon streams.
- b) Amine cracking is a form of alkaline stress corrosion cracking (ASCC).
- c) It is most often found at or adjacent to non-postweld-heat-treated (non-PWHT'd) carbon steel welds or in highly cold worked parts.
- d) Amine cracking should not be confused with several other types of SCC that can occur in amine environments, which are further described in [3.66](#) and [3.12](#).

3.3.2 Affected Materials

Carbon steel and low-alloy steels.

3.3.3 Critical Factors

- a) The critical factors are the level of tensile stress, the type of amine, and temperature.
- b) Increasing stress level increases the likelihood and severity of cracking. Cracking is most often associated with high residual stresses from welding or cold working that have not been removed by an effective stress-relieving heat treatment.
- c) Cracking is more likely to occur in MEA and DEA services, but is also found in most amines including MDEA and DIPA (ADIP).
- d) Increasing temperature increases the likelihood and severity of cracking; however, cracking has been reported down to ambient temperatures with some amines, MEA in particular. Other than in special cases (such as where the steel component is completely clad or overlaid with stainless steel or other alloy and the welds are not exposed), PWHT is now commonly recommended for all lean amine systems (excluding fresh amine) at all operating temperatures, regardless of amine type. Some refiners also PWHT'd rich amine service equipment, whether for amine SCC resistance, wet H_2S [SSC and stress-oriented hydrogen-induced cracking (SOHIC)] resistance, or both. Refer to API 945 for guidelines on PWHT for various amine services.
- e) Amine cracking is most often associated with lean amine services, where a solution of amine and water is used. The pure alkanolamine does not cause cracking. In rich amine services in H_2S removal systems, the H_2S helps form an iron sulfide (FeS) film on steel surfaces that helps impede amine SCC. Cracking in rich amine services is most often associated with wet H_2S . (See [3.67](#).)
- f) Cracking can occur in non-PWHT'd piping and equipment as the result of exposure to steam out and to short-term amine carryover. This is another reason PWHT (for stress relief) is now commonly recommended regardless of operating temperature.
- g) Amine concentration does not appear to have a significant effect on the propensity for cracking.

3.3.4 Affected Units or Equipment

All non-PWHT'd carbon steel piping and equipment in amine service, including contactors, absorbers, strippers, filters, regenerators, and heat exchangers, as well as any equipment subject to amine carryover, are subject to cracking. Equipment in rich amine service is less susceptible than equipment in lean amine service, but not necessarily immune, especially vessels where acid gas is either entering the amine (making rich amine) or leaving the amine (making lean amine).

3.3.5 Appearance or Morphology of Damage

- a) Amine SCC cracks initiate on the (process side) surface of piping and equipment, primarily at welds. Cracks can appear in the HAZ and/or the weld metal but are most often found in the high residual stress zone, which is typically beyond the metallurgical HAZ, about a tenth of an inch or more (several millimeters) from the weld. (Figure 3-3-1)
- b) Cracking typically develops parallel to the weld, and there may be multiple parallel cracks. In weld metal, the cracks are either longitudinal or transverse to the weld.
- c) At set-on nozzles, the cracks are radial in the base metal, i.e. they fan out from the bore. (Figure 3-3-2)
- d) At set-in nozzles, the cracks are usually parallel to the weld.
- e) The appearance of the cracks on the surface may be similar to those caused by wet H₂S cracking.
- f) Because residual stress is a driving force for cracking, cracks can occur on the process side opposite external attachment welds.
- g) Positive identification of amine cracking can be confirmed by metallographic analysis. The cracking is typically intergranular and oxide filled with some branching. (Figure 3-3-1 and Figures 3-3-3 to 3-3-5)

3.3.6 Prevention/Mitigation

- a) Carbon steel welds in piping and equipment should be stress relieved in accordance with API 945 and NACE SP0472. The recommended minimum stress-relief temperature is 1175 ± 25 °F (635 ± 15 °C). The same recommendation applies to repair welds and to internal and external attachment welds. (See Figure 3-3-6.) For local PWHT, recommended heat treatment band width is listed in NACE SP0472 with reference to WRC 452.
- b) Consider using solid or clad stainless steel or other corrosion-resistant alloys in lieu of carbon steel.
- c) Thoroughly water wash non-PWHT'd carbon steel piping and equipment prior to welding, heat treatment, or steam out.

3.3.7 Inspection and Monitoring

- a) Wet fluorescent magnetic particle testing (WFMT), alternating current field measurement (ACFM), and eddy current testing (ECT) can be effective techniques to detect these surface-breaking cracks. Proper surface preparation by grit blasting, high-pressure water blasting, flapper wheel abrasive grinding, or other method is required to remove scale and contaminants. The method of surface preparation is dependent upon the specific technique.
- b) Angle beam [shear wave ultrasonic testing (SWUT) and phased array ultrasonic testing (PAUT)] ultrasonic techniques can be effective to detect and size cracks and would be the methods typically used for piping; however, caution must be exercised when interpreting results on piping welds that have not previously been inspected with angle beam UT (SWUT or PAUT) as it may be difficult to distinguish SCC from original fabrication flaws. SWUT and PAUT can also be used to periodically monitor crack growth.
- c) Liquid penetrant testing (PT) may be used but should not be the only means of detection. PT may not be effective in finding tight cracks because the cracks are oxide filled.
- d) RT may not be effective in detecting fine, tight cracks.
- e) Acoustic emission testing (AET) can be used for locating cracks and monitoring crack growth.

3.3.8 Related Mechanisms

Caustic SCC (3.15) and carbonate SCC (3.12) are other forms of ASCC that are similar in appearance. Ammonia SCC of carbon steel (3.4) is also similar in appearance.

3.3.9 References

1. API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*, American Petroleum Institute, Washington, DC.
2. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.
3. J. Gutzeit and J.M. Johnson, "Stress Corrosion Cracking of Carbon Steel Welds in Amine Service," *Materials Performance*, Vol. 25, No. 7, 1986, p.18.
4. J.P. Richert et al., "Stress Corrosion Cracking of Carbon Steel in Amine Systems," Paper No. 187, *Corrosion/87*, NACE International, Houston, TX.
5. A. Bagdasarian et al., "Stress Corrosion Cracking of Carbon Steel in DEA and ADIP Solutions," *Materials Performance*, 1991, pp. 63–67.
6. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.
7. WRC Bulletin 452, *Recommended Practices for Local Heating of Welds in Pressure Vessels*, Welding Research Council, Shaker Heights, OH, June 2000.

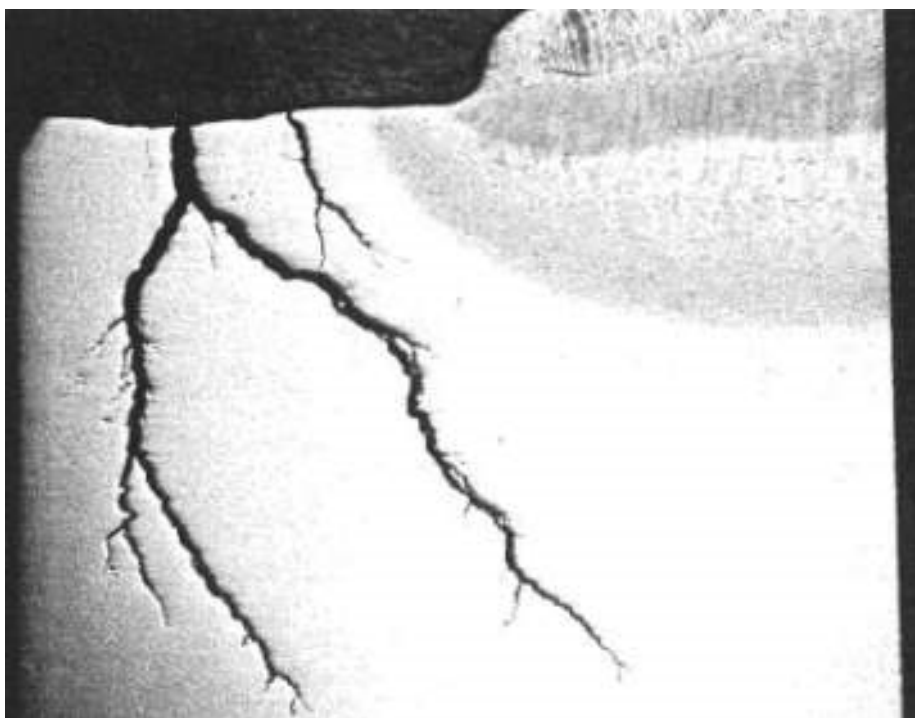


Figure 3-3-1—A photomicrograph of a cross section of a weld in non-PWHT'd carbon steel piping showing amine SCC in the vicinity of a piping weld. Magnification 6X (from API 945).



Figure 3-3-2—Radial amine SCC cracks emanating from the bore of a nozzle in a rich amine reboiler exchanger.

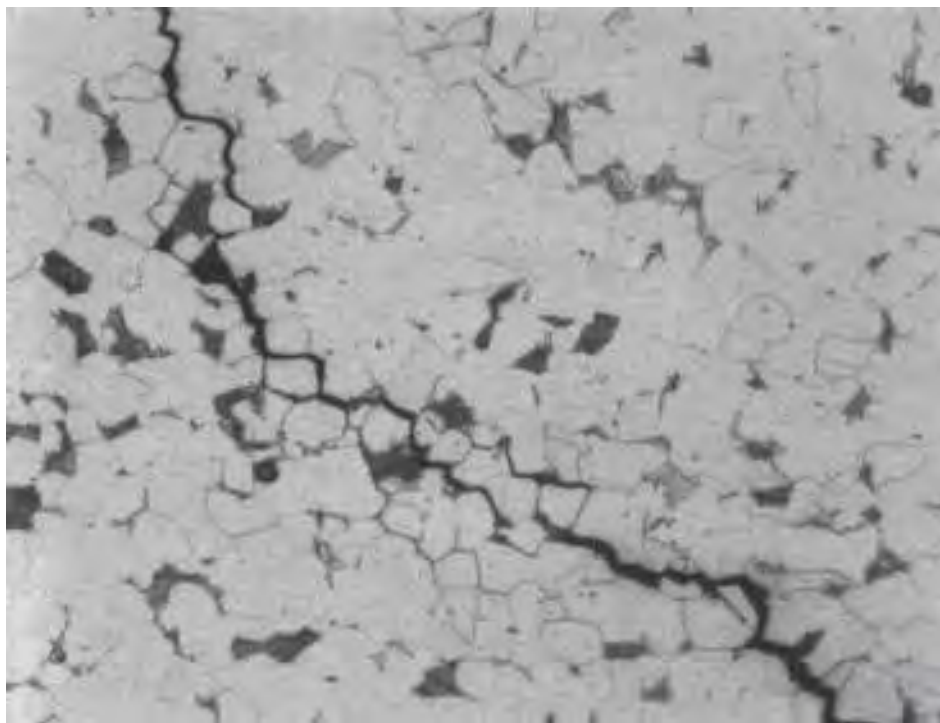


Figure 3-3-3—A higher-magnification view of the crack tip in Figure 3-3-1. Magnification 200X (from API 945).

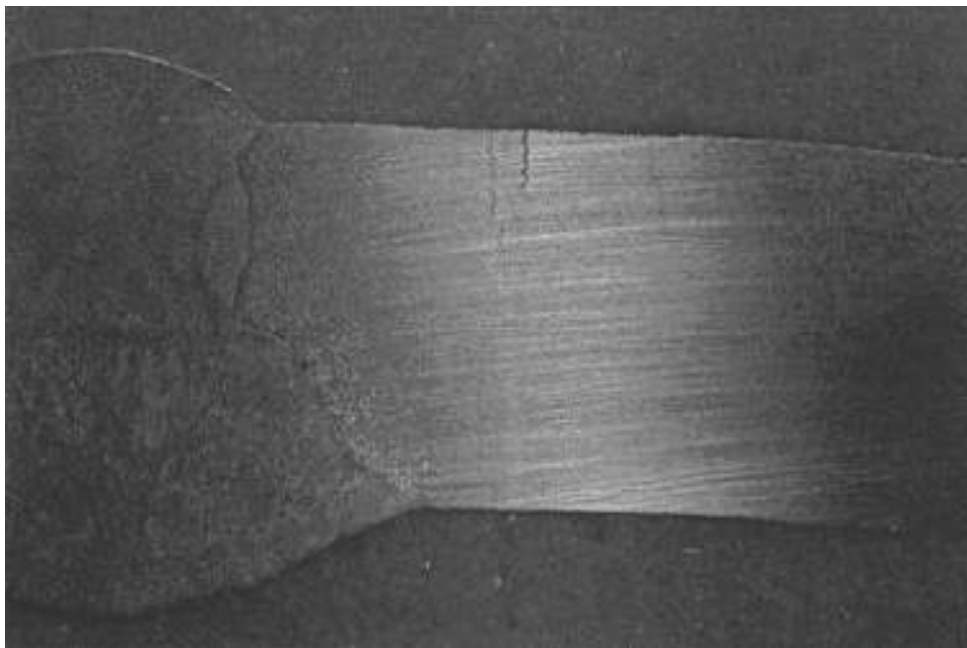


Figure 3-3-4—A photomicrograph of a cross section of a carbon steel piping weld showing amine SCC in a section of the line from the MEA absorber column normally operated at 100 °F (38 °C). Magnification 6X (from API 945).

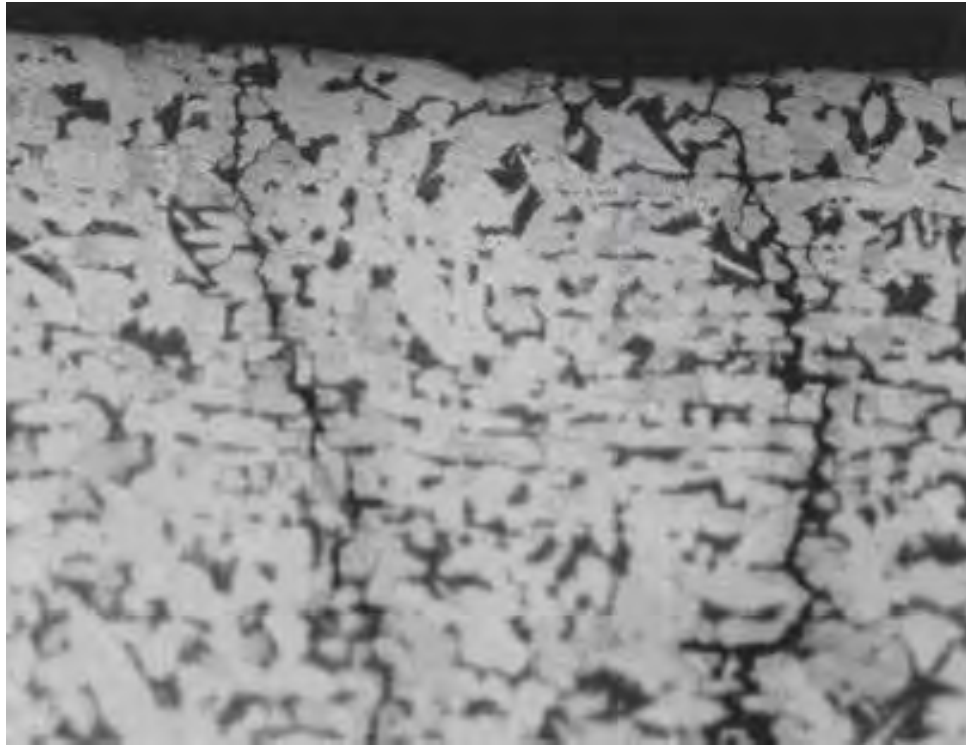


Figure 3-3-5—A higher-magnification view of the cracks in Figure 3-3-4, which illustrates the intergranular nature of the cracking. Magnification 200X (from API 945).

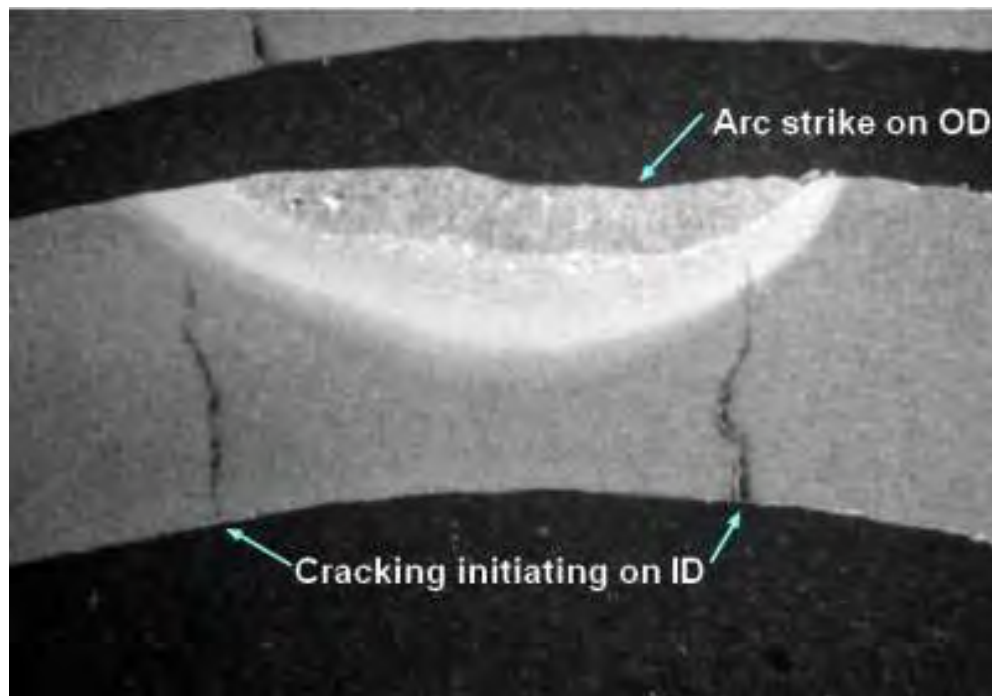


Figure 3-3-6—Amine SCC developed on the inside diameter (ID) beneath an arc strike on the outside diameter (OD) of a 3-in. line in 20 % MEA. The original line was PWHT'd during original fabrication but not the arc strike. Leaks occurred after 30 years of service.

3.4 Ammonia Stress Corrosion Cracking

3.4.1 Description of Damage

- a) Aqueous streams containing ammonia may cause SCC in some copper alloys.
- b) Carbon steel is susceptible to SCC in anhydrous ammonia.

3.4.2 Affected Materials

- a) Copper-zinc alloys (brasses, especially as zinc increases above 15 %), including admiralty brass and aluminum brasses, in environments with aqueous ammonia and/or ammonium compounds.
- b) Carbon steel, especially high-strength steel, in anhydrous ammonia.

3.4.3 Critical Factors

- a) For copper alloys:
 - 1. susceptible alloys may suffer cracking under the combination of residual stress and exposure to ammoniated chemical compounds;
 - 2. zinc content of brasses affects susceptibility, especially as zinc increases above 15 %;
 - 3. a water phase with ammonia or ammoniacal compounds must be present;
 - 4. oxygen is necessary, but trace amounts are sufficient;
 - 5. pH needs to be above 8.5;
 - 6. occurs at any temperature;
 - 7. residual stresses from fabrication or tube rolling are sufficient to promote cracking.
- b) For steel:
 - 1. anhydrous ammonia with < 0.2 % water may cause cracking in carbon steel;
 - 2. cracking has been reported as low as -27 °F (-33 °C) in laboratory testing; crack growth rates and cracking susceptibility increase with increasing temperature, but cracking can occur at ambient or refrigerated conditions;
 - 3. stress relief after welding eliminates susceptibility of most common steels (those not greater than 70 ksi minimum specified tensile strength);
 - 4. contamination with even small amounts of air or oxygen increases tendency toward cracking;
 - 5. high residual stresses from fabrication and welding increase susceptibility.

3.4.4 Affected Units or Equipment

- a) Copper-zinc alloy tubes in heat exchangers.
 - 1. Ammonia is present as a process contaminant in some services or may be intentionally added as an acid neutralizer.
 - 2. Ammonia can be present in cooling water.
 - 3. Ammonia can be present in steam condensate and boiler feedwater (BFW) systems. Some chemicals used for treating BFW, including hydrazine, neutralizing amines, and ammonia-containing compounds, can lead to SCC if not properly controlled.

- b) Non-stress-relieved carbon steel ammonia storage tanks, piping, and equipment in ammonia refrigeration units, as well as some lube oil refining processes.

3.4.5 Appearance or Morphology of Damage

a) Copper alloys.

1. Surface-breaking cracks may show bluish corrosion products.
2. Exchanger tubes show single or highly branched cracks on the surface.
3. Cracking can be either transgranular (Figure 3-4-1 and Figure 3-4-2) or intergranular (Figure 3-4-3), depending on the environment and stress level.

b) Carbon steel.

1. Cracking will occur at exposed non-stress-relieved welds and HAZs.
2. Cracking is primarily intergranular in nature.

3.4.6 Prevention/Mitigation

a) Copper alloys.

1. Copper-zinc alloys with < 15 % zinc have improved resistance.
2. The 90-10 Cu-Ni and 70-30 Cu-Ni alloys have very low susceptibility. Below 120 °F (50 °C), the cupro-nickels are immune for all practical purposes.
3. SCC in steam service can sometimes be controlled by preventing the ingress of air.
4. 300 series SS and nickel-based alloys are immune.

b) Carbon steel.

1. SCC of steel can be prevented through the addition of small quantities of water to the ammonia (0.2 % minimum). Be aware that vapor spaces could have less than 0.2 % water present due to partitioning of ammonia in water phase.
2. An effective stress relief of the welds reduces residual stress to the point where ammonia SCC can be prevented.
3. Low-strength steels (<70 ksi minimum specified tensile strength) should be used.
4. Prevent ingress of oxygen into storage facilities. Even low levels of oxygen (<5 ppm) have been reported to lead to cracking under some conditions. Oxygen levels should be maintained below 1 ppm.
5. Nitrogen can be used to purge oxygen prior to introduction of ammonia into atmospheric and pressurized storage systems.

3.4.7 Inspection and Monitoring

a) For copper alloys:

1. the pH and ammonia content of water draw samples should be monitored to assess susceptibility of copper alloys to determine extent of inspection;
2. heat exchanger tubes can be monitored for cracking using ECT or VT. PT can be applied in the rolled area, which is highly susceptible to cracking.

- b) For carbon steel storage tanks (atmospheric or pressurized), vessels, and piping, in anhydrous ammonia:
1. WFMT is typically used on the welds and HAZs of storage tanks and pressure vessels and can also identify SCC in piping; alternatively, eddy current array testing can be used to perform these inspections;
 2. angle beam UT (SWUT or PAUT) can be performed from the outside surface;
 3. AET can be used for locating cracks and monitoring crack growth in vessels.

NOTE NH_3 SCC can occur parallel, transverse, or oblique to the weld and HAZ. NDE applied should be performed to detect various orientations of SCC.

3.4.8 Related Mechanisms

None.

3.4.9 References

1. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, p. 117.
2. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
3. A. Cohen, "Copper and Copper-base Alloys," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 479–501.
4. NACE Publication 5A192, *Integrity of Equipment in Anhydrous Ammonia Storage and Handling*, NACE International, Houston, TX, 2004.
5. "Environmental Cracking," Materials Technology Institute, St. Louis, Missouri, 2016.

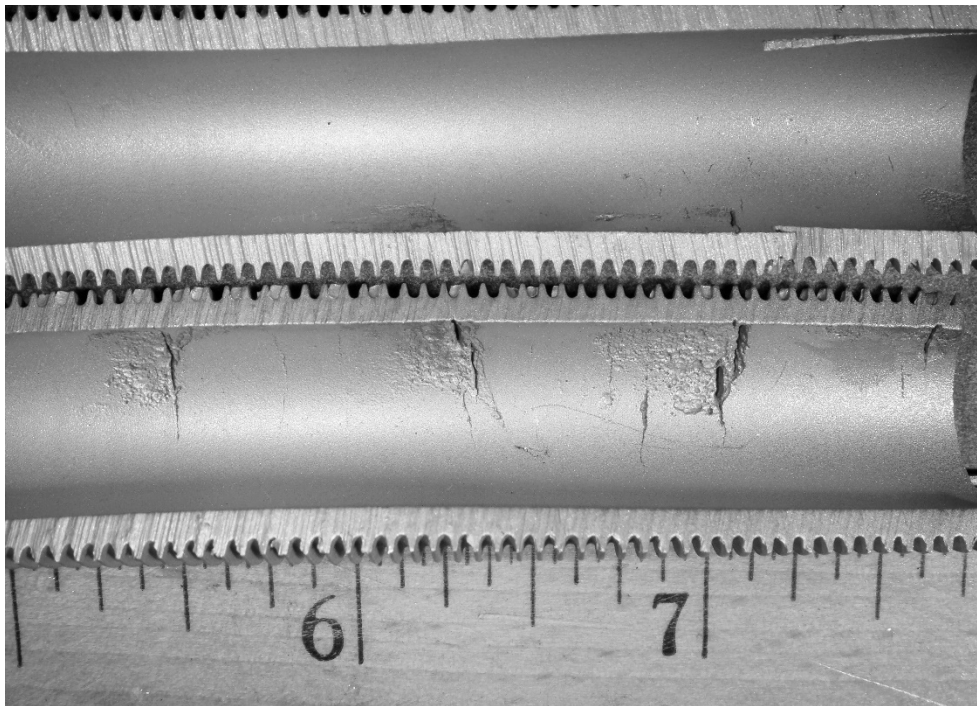


Figure 3-4-1—Ammonia SCC in an inhibited admiralty tube UNS C44300, 0.75 in. diameter, BWG 16 (0.063 in. thick) with extruded fins.

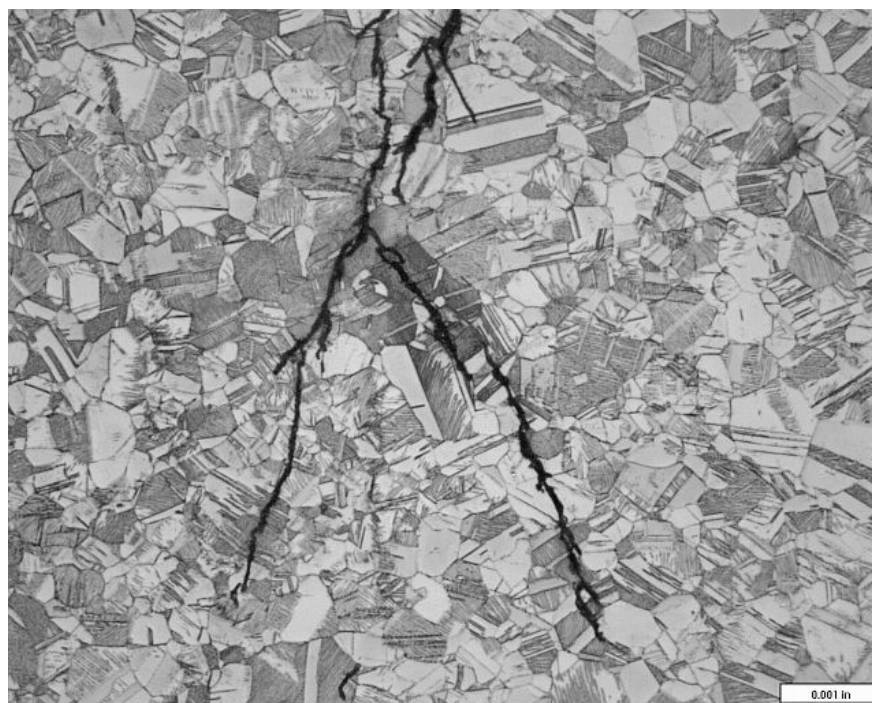


Figure 3-4-2—High-magnification view of a cross section of the tube in Figure 3-4-1 showing transgranular cracking. (Magnification 500X.)

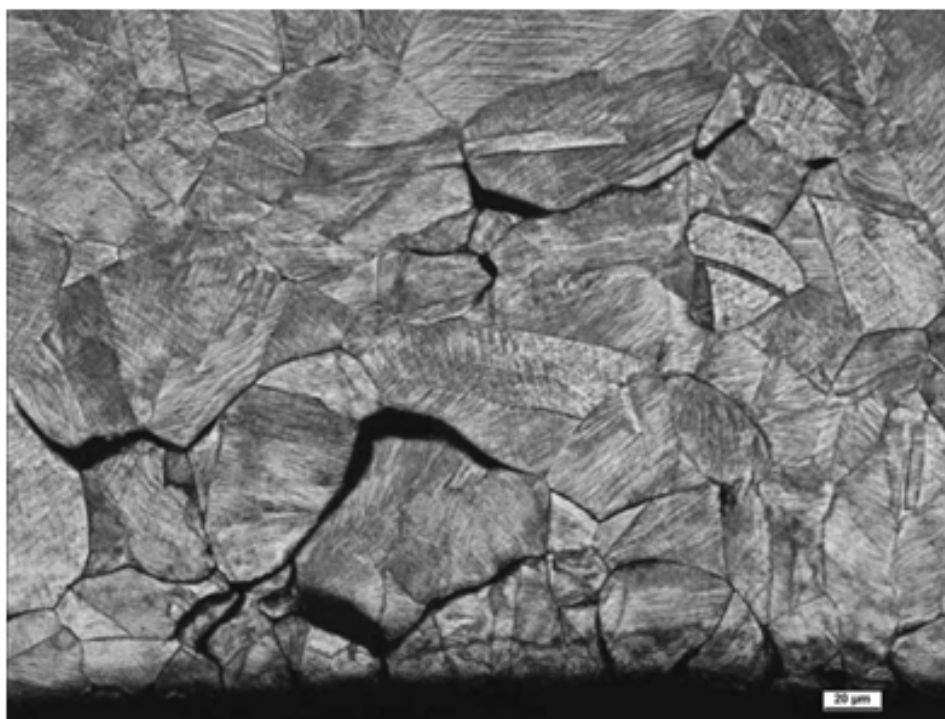


Figure 3-4-3—High-magnification view of a cross section of a brass exchanger tube showing intergranular cracking.

3.5 Ammonium Bisulfide Corrosion (Alkaline Sour Water)

3.5.1 Description of Damage

Aggressive corrosion occurring in hydroprocessing reactor effluent streams and in units handling alkaline sour water (SW), especially in areas of high turbulence.

3.5.2 Affected Materials

- a) Carbon steel and low-alloy steels.
- b) 300 series SS, duplex stainless steel, nickel-based alloys, and titanium and its alloys are more resistant, depending on ammonium bisulfide (NH_4HS) concentration and velocity.
 - 1. Aluminum has been used for NH_4HS corrosion resistance in air coolers, but can suffer high corrosion rates in high-velocity or turbulent locations.
 - 2. Titanium and its alloys have been used for NH_4HS corrosion resistance in air coolers but can suffer embrittlement from hydriding in these services. (See 3.66.)
 - 3. Welds in duplex stainless steel can be susceptible to SSC. (See 3.67 and API 582.)
- c) NH_4HS rapidly corrodes admiralty brass tubes and other copper alloys.

3.5.3 Critical Factors

- a) NH_4HS concentration, H_2S partial pressure, velocity (i.e. wall shear stress), and/or localized turbulence, pH, temperature, alloy composition, and flow distribution are all critical factors to consider.
- b) Corrosion increases with increasing NH_4HS concentration and increasing velocity (i.e. wall shear stress). For carbon steel, solutions below 2 wt % NH_4HS are not generally corrosive. Above 2 wt %, solutions are increasingly corrosive.
- c) In hydroprocessing reactors, nitrogen in the feed is converted to ammonia and reacts with H_2S to form NH_4HS . NH_4HS precipitates out of the gas phase in the reactor effluent stream when temperatures drop to within the range of 120 °F to 150 °F (50 °C to 65 °C), depending on the concentration of NH_3 and H_2S , and may cause fouling and plugging unless flushed away with wash water. A similar reaction between NH_3 and H_2S occurs in FCC and coker units, leading to precipitation in the associated fractionator overheads.
- d) NH_4HS salt deposits can lead to under-deposit corrosion and fouling. The salts are not corrosive unless they become hydrated at which point they become corrosive.
- e) Oxygen and iron in the wash water injected into hydroprocessing reactor effluent can lead to increased corrosion and fouling.
- f) The presence of cyanides increases the severity of corrosion in FCC gas plants, coker gas plants, and sour water stripper (SWS) overheads by diminishing the protection afforded by the normally protective sulfide film.

3.5.4 Affected Units or Equipment

- a) Hydroprocessing units.
 - 1. Several major failures have occurred in hydroprocessing reactor effluent systems due to localized corrosion.
 - 2. Fouling and/or velocity accelerated corrosion may be found at:
 - air cooler header boxes;

- inlet and outlet piping of air coolers;
- exchanger tubes, especially at the inlet and outlet;
- effluent separators and piping into and out of the reactor effluent separators;
- SW draw piping from reactor effluent separators, especially downstream of control valves where flashing may cause severe erosion-corrosion ([Figure 3-5-1](#));
- vapor lines from the high-pressure separator due to entrained or condensed SW;
- hydrocarbon lines from reactor effluent separators due to entrained SW; and
- stripper column overheads containing SW.

b) FCC units.

NH₄HS concentrations are usually less than 2 wt %, but high velocities and/or the presence of cyanides can damage protective iron sulfide scales.

c) SWSs.

High concentrations of NH₄HS and the possible presence of cyanides can lead to corrosion in stripper overhead piping, condensers, and accumulator and reflux piping.

d) Amine units.

High concentrations of NH₄HS may be found in regenerator overheads and reflux piping depending on unit operation.

e) Delayed cokers.

High concentrations of NH₄HS may be found in the gas concentration plant downstream of the fractionator tower.

3.5.5 Appearance or Morphology of Damage

- a) General loss in thickness of carbon steel, with the potential for extremely high localized rates of wall loss at changes in direction or turbulent flow areas above 2 wt % concentration. Generalized corrosion, especially if combined with high unit pressure, can lead to rupture failure.
- b) High localized corrosion rates have also been seen in straight runs of piping, so locating the site of the worst corrosion can be a challenge.
- c) Low velocities may result in extremely localized under-deposit corrosion if sufficient water is not available to dissolve the NH₄HS salts that precipitated.
- d) Heat exchangers may show plugging and loss of duty due to fouling.

3.5.6 Prevention/Mitigation

- a) Good design practice includes symmetrical and hydraulically balanced flow in and out of air-cooled exchangers.
- b) Carefully review design and localized velocities as process conditions change, particularly as NH₄HS concentrations exceed 2 wt % and begin to approach 8 wt % or higher.
- c) Use resistant materials of construction (e.g. duplex stainless steel, Alloy 825) at velocities above 20 fps (6 m/s), depending on NH₄HS concentration.

- d) Properly design and maintain water wash injection with low oxygen content; provide sufficient excess water to ensure that an adequate amount of water remains as liquid to dilute the NH_4HS salts. Use proper injection spray nozzles and metallurgy.
- e) Titanium and Alloy C276 have been used in overhead condensers in SWS units.
- f) Aluminum exchanger tubes are extremely susceptible to erosion-corrosion damage.

3.5.7 Inspection and Monitoring

- a) Ammonium bisulfide corrosion can be highly localized and difficult to locate.
- b) Determine ammonium bisulfide content through sampling or calculation.
- c) UT scanning and/or RT thickness measurement should focus on areas of turbulence and areas of high and low velocity.
 - 1. Special attention should be given to water injection locations in areas of expected water impact (injection point inspection).
 - 2. UT downstream of control valves that see high NH_4HS concentrations.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Guided wave testing (GWT) can be used as a screening tool.
- f) For steel (magnetic material) air cooler tubes (which are normally finned), internal rotating inspection system (IRIS), magnetic flux leakage (MFL), near-field testing (NFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.
- g) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, remote field testing (RFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.
- h) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of damage or distortion.

3.5.8 Related Mechanisms

Erosion/erosion-corrosion (3.27), ammonium chloride corrosion (3.6), concentration cell corrosion (3.19), titanium hydriding (3.66), and chloride SCC (Cl^- SCC) (3.17).

3.5.9 References

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12. S. Srinivasan, R.J. Horvath, K.M. Yap, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions—Part 3," Paper No. 08929, *Corrosion/2017*, NACE International, Houston, TX.

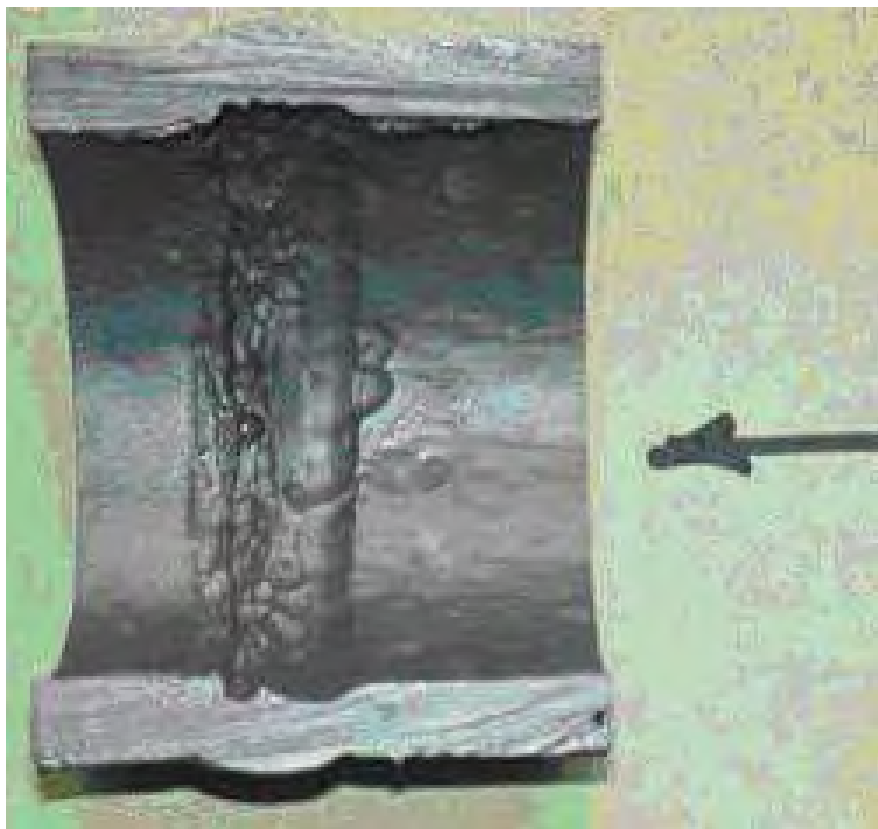


Figure 3-5-1—Ammonium bisulfide corrosion in a 2-in. CS elbow and straight section in a SW line off the cold high-pressure separator (HPS) in an HDT unit.

3.6 Ammonium Chloride and Amine Hydrochloride Corrosion

3.6.1 Description of Damage

Localized corrosion, often pitting, normally occurring under ammonium chloride or amine salt deposits, often in the absence of a free water phase.

3.6.2 Affected Materials

All commonly used materials are susceptible. In order of increasing resistance: carbon steel and low-alloy steels; 300 series SS; duplex stainless steel and Alloys 400, 800, and 825; Alloys 625 and C276; and titanium.

3.6.3 Critical Factors

- a) Concentrations of NH_3 , hydrochloric acid (HCl), and amine salts; temperature; and water availability are the critical factors.
- b) Ammonium chloride salts may precipitate from high-temperature streams as they are cooled, depending upon the concentration of NH_3 and HCl, and may corrode piping and equipment at temperatures well above the water dew point. Salting has been observed up to approximately 400 °F (205 °C).
- c) Ammonium chloride salts are hygroscopic and readily absorb water. A small amount of water can lead to very aggressive corrosion [>100 mpy (>2.5 mm/yr)].
- d) Ammonium chloride is highly water soluble, highly corrosive, and forms an acidic solution when mixed with water. Neutralizing amines can also react with hydrogen chloride to form amine hydrochlorides that can act in a similar fashion.
- e) Corrosion rates increase with increasing temperature.
- f) When the salts deposit above the water dew point, a water wash injection may be required to dissolve them.

3.6.4 Affected Units or Equipment

- a) Crude tower overheads.
 1. Tower top, top trays, and overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low-flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.
 2. Top pumparound streams may be affected if ammonia or amine chloride salts are present.
- b) Hydroprocessing.
 1. Reactor effluent streams are subject to ammonium chloride salt fouling and corrosion. Water washing may be required if exchanger fouling or loss in duty occurs.
- c) Catalytic reforming.
- d) Reactor effluent streams and the H_2 recycle system are subject to ammonium chloride salting and corrosion.
- e) FCC unit and coker fractionator overheads.
 1. Overhead systems and top pumparounds are subject to ammonium chloride corrosion and salting.

3.6.5 Appearance or Morphology of Damage

- a) The salts have a whitish, greenish, or brownish appearance. Water washing and/or steam out will remove deposits so that evidence of fouling may not be evident during an internal VT.
- b) Corrosion underneath the salts is typically very localized and can result in pitting.
- c) Corrosion rates can be extremely high.

3.6.6 Prevention/Mitigation

Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts, but even the most corrosion-resistant nickel-based alloys and titanium alloys may suffer pitting corrosion.

- a) Crude unit.
 - 1. Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.
 - 2. A water wash may be required in the crude tower overhead line to flush the salt deposits.
 - 3. Filming amine inhibitors are often added to control corrosion but may not reach metal surfaces under deposits that have already formed.
- b) Hydroprocessing.
 - 1. Limit chlorides in the hydrocarbon feed to the reactor.
 - 2. Limit chlorides in the make-up hydrogen supply.
 - 3. A continuous or intermittent water wash may be required in the reactor effluent stream to flush out the salt deposits or, preferably, prevent them from forming.
 - 4. Monitoring of the feed streams and effluent waters will give an indication of the amount of ammonia and chlorides present; however, process simulation may be required to determine the concentrations and dew point temperatures. If the ammonium chloride salt deposition temperature has been calculated, temperature monitoring and control may be effective for maintaining metal temperatures above the salt deposition temperature.
- c) Catalytic reforming.
 - 1. Net hydrogen produced can be treated in alumina bed chloride traps to remove chlorides.
 - 2. Water washing has been used in some cases, but the system must be carefully designed.
 - 3. Some tower overheads may require neutralizing or filming amines.
- d) FCC and coker units.
 - 1. Continuous water wash in overheads is usually used to dissolve salts as they form.
 - 2. Intermittent water wash can be used to remove salt deposits from fractionator trays. This usually requires "slumping" the column and re-running of affected cuts.

3.6.7 Inspection and Monitoring

- a) Ammonium chloride corrosion can be highly localized and difficult to locate. Salts are often mobile, depending on size of accumulation and hydration, causing them to flow with hydraulic traffic and gravity.

- b) RT or UT scanning methods [automated ultrasonic testing (AUT), manual close-grid, scanning UT] can be used to determine remaining wall thickness. These methods are preferred over typical spot UT thickness monitoring because the corrosion is so highly localized.
- c) GWT can be used as a screening tool.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of distortion or other damage.
- f) The presence of deposits is often detected when the pressure drop increases or the thermal performance of exchangers has deteriorated.
- g) Corrosion probes or coupons can be useful, but the salt must deposit on the corrosion probe element to detect the corrosion.
- h) For steel (magnetic material) air cooler tubes (which are normally finned), IRIS, MFL, NFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.
- i) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, RFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

3.6.8 Related Mechanisms

Hydrochloric acid corrosion (3.37), Cl^- SCC (3.17), aqueous organic acid corrosion (3.7), and concentration cell corrosion (3.19).

3.6.9 References

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5. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.
6. NACE Publication 34109, *Crude Distillation Unit—Distillation Tower Overhead System Corrosion*, NACE International, Houston, TX, 2009.
7. API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*, American Petroleum Institute, Washington, DC.

3.7 Aqueous Organic Acid Corrosion

3.7.1 Description of Damage

Organic compounds present in some crude oils decompose in the crude furnace to form low molecular weight organic acids (Table 3-7-1) that are soluble in water. They may also result from additives used in upstream operations or desalting. These acids can contribute significantly to aqueous corrosion depending on the type and quantity of acids and the presence of other contaminants, particularly if they condense in distillation tower overhead systems. They can also cause corrosion at mix points where recovered oil streams are injected.

3.7.2 Affected Materials

- a) Carbon steel and low-alloy steels are affected.
- b) Most corrosion-resistant alloys used in crude tower overhead systems are generally not affected.
 - 1. Austenitic stainless steels are generally resistant, but this mechanism is often associated with streams that cause inorganic acid corrosion as well as pitting and SCC due to halogens (e.g. chlorides), so their use should be avoided unless it is known that halogens are not present.

3.7.3 Critical Factors

- a) Corrosion is a function of the type and quantity of organic acids, metal temperature, fluid velocity, system pH, and presence of other acids.
- b) The low-molecular-weight organic acids that are formed include formic acid, acetic acid, propionic acid, and butyric acid.
- c) The lower-molecular-weight acids such as formic acid and acetic acid are the most corrosive. They are soluble in naphtha and are extracted into the water phase, once the water condenses, and contribute to a reduction of pH.
- d) The presence of organic acids will contribute to the overall demand for neutralizing chemicals, but their effects may be completely masked by the presence of other acids such as HCl, H₂S, carbonic acid, and others.
- e) Corrosion is most likely to be a problem where relatively “non-corrosive” conditions have existed in an overhead system. When there is a sudden increase in low molecular weight organic acids, it can reduce the pH of the water in the overhead system and cause a potentially unexpected increase in neutralizer demand.
- f) The type and quantity of organic acids formed in the overhead system are crude specific. One source of these acids is believed to be the thermal decomposition of naphthenic acids in the crude, which may be precursors to light organic acid formation. In that case, the processing of higher total acid number (TAN) crudes might increase organic acid in the overheads. However, very little published information is available on this subject.
- g) Some higher molecular weight organic acids condense above the water dew point in overhead systems, but they are generally not present in sufficient quantities to cause corrosion.
- h) Light organic acids such as acetic acid are sometimes added during oilfield operations, e.g. in dehydrators or desalters to improve performance and inhibit calcium naphthenate salt deposition. (Reference 2) Such acids will vaporize in the crude preheat exchangers and furnace and go up the column into the crude tower overhead system.
- i) Other, high molecular weight acids used as oilfield additives can thermally decompose at crude unit temperatures to form volatile, corrosive light organic acids such as acetic and formic acids.
- j) In general, light organic acids do not generate the severity of corrosion associated with inorganic acids such as HCl. Table 3-7-1 shows the HCl equivalent factor for corrosion by organic acids in overhead systems. To calculate the HCl equivalent of an organic acid, multiply the content of the organic acid (in weight ppm) by the factor for that acid, and the result will be the equivalent content of HCl (in ppmw). This number can then be used to estimate the additional neutralizer needed in the overhead system to compensate for the organic acids present. This must be done with caution, because excess neutralizer can lead to amine hydrochloride salts in overhead systems.

3.7.4 Affected Units or Equipment

- a) All carbon steel piping and process equipment in crude tower, vacuum tower, visbreaker, and coker fractionator overhead systems including heat exchangers, towers, and drums are susceptible to corrosion where acidic conditions occur.
- b) Localized corrosion can occur at mix points from recovered oil streams when wet streams combine with streams contaminated with organic acid.
- c) Corrosion tends to occur where water accumulates or where hydrocarbon flow directs water droplets against metal surfaces. Examples include the bottoms of overhead separator drums and exchanger shells or channels, the boots of separator drums, and liquid hold-up areas on trays.
- d) In horizontal piping, organic acid corrosion is generally found both in the vapor space where liquid water can condense and along the bottom of the piping where liquid water may run.
- e) Corrosion is also sensitive to flow rate and will tend to be more severe in higher-velocity and turbulent areas in piping systems such as elbows, tees, downstream of pumps, and downstream of control valves. Other areas of potentially more severe corrosion due to velocity and turbulence include overhead transfer lines, overhead condensers and separator drums, and exchanger tubes.

3.7.5 Appearance or Morphology of Damage

- a) Aqueous organic acid corrosion will result in thinning. General and local wall loss can be expected. In carbon steels, local losses are observed where a water phase is being formed such as during condensation or separation.
- b) Light organic acid corrosion typically leaves the corroded surface smooth and damage may be difficult to distinguish from corrosion by other acids in the overhead system. It is sometimes mistaken for HCl corrosion or carbonic acid (CO_2) corrosion.
- c) In pipe or other equipment where there is significant flow, the surfaces are sometimes smoothly grooved.
- d) Localized pitting occurs in low-velocity or condensing conditions.

3.7.6 Prevention/Mitigation

- a) Corrosion caused by light organic acids in crude unit overhead systems can be minimized through the injection of an acid-neutralizing additive. However, problems may arise when frequent changes in crude blends lead to frequent changes in neutralizer demand.
- b) The TAN of the crudes being processed can be used as an initial guide to determine the neutralizer requirement. If the crude TAN increases, one should anticipate an increase in the acid concentration in the overhead system.
- c) After a new crude is processed, a review of analyses of water samples from the boot of the overhead separator drum can be used to determine how much light organic acid reaches the overhead system and thereby optimize future neutralizer additions.
- d) Filming amines can also be used to prevent corrosion if the filming amine selected does not react with the organic acid. However, filming amines are generally not as effective as neutralization in mitigating overhead system corrosion.
- e) Upgrading to corrosion-resistant alloys will prevent organic acid corrosion, but the selection of suitable materials should account for other potential damage mechanisms in the overhead system.

3.7.7 Inspection and Monitoring

- a) Various UT and RT techniques can be used to assess metal loss.
- b) GWT and electromagnetic acoustic transducer (EMAT) can be utilized to screen for wall loss.
- c) Corrosion probes and corrosion coupons have proven valuable, especially in conjunction with water sample analysis.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Infrared thermography scanning can also be used to detect locations where liquid water may exist and in this way supplement other NDE methods.
- f) The pH should be monitored where water is known to accumulate in the process, particularly at the overhead accumulation drum of the crude tower. If a low pH is found that cannot be accounted for by the level of chlorides measured, additional acids, potentially including organic acids, are likely present.

3.7.8 Related Mechanisms

HCl corrosion (3.37) and naphthenic acid corrosion (NAC) (3.46).

3.7.9 References

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2. S. Kapusta, F. van den Berg, R. Daane, and M.C. Place, "The Impact of Oil Field Chemicals on Refinery Corrosion Problems," Paper No. 03649, *Corrosion/2003*, NACE International, Houston, TX.
3. S. Lordo, J.M. Garcia, and S. Garcia-Swofford, "Desalter Acidification Additives and Their Potential Impacts on Crude Units," Paper No. 08556, *Corrosion/2008*, NACE International, Houston, TX.
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6. J.R. Rue and D.P. Naeger, "Advances in Crude Unit Corrosion Control," Paper No. 87199, *Corrosion/87*, NACE International, Houston, TX.
7. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.

Table 3-7-1—Light Organic Acid Corrosion Equivalency Factors

Acid	HCl Equivalent Factor
Formic	0.76
Acetic	0.61
Propionic	0.49
Methyl propionic	0.41
Butanoic	0.41
3-methyl butanoic	0.36
Pentanoic	0.36
Hexanoic	0.31
Heptanoic	0.28

3.8 Atmospheric Corrosion

3.8.1 Description of Damage

Corrosion that occurs from moisture associated with atmospheric conditions. Marine environments and moist, polluted industrial environments with airborne contaminants are the most severe. Dry rural environments cause very little corrosion.

3.8.2 Affected Materials

Carbon steel, low-alloy steels, and copper alloyed aluminum.

3.8.3 Critical Factors

- a) The physical location of the plant (industrial, marine, urban, rural).
- b) The amount of moisture (humidity, rainfall) typically present or the presence of cooling tower mist.
- c) The presence of salts, sulfur compounds, dirt, or other contaminants in the air.
- d) Chlorides, H₂S, fly ash, and other airborne contaminants from cooling tower and wet gas scrubber drift, furnace stacks, and other equipment accelerate corrosion.
- e) Orientation to the prevailing wind and rain.
- f) Corrosion rates increase with temperature up to about 250 °F (120 °C). Above 250 °F (120 °C), surfaces are usually too dry for corrosion to occur except under insulation. (See [3.22.](#))
- g) Designs that trap water or moisture in crevices or other configurations are more prone to attack.
- h) Marine environments can be very corrosive (about 20 mpy) as are industrial environments that contain acids or sulfur compounds that can form acids (about 5 mpy to 10 mpy).
- i) Inland locations exposed to a moderate amount of precipitation or humidity are considered moderately corrosive environments (about 1 mpy to 3 mpy).
- j) Dry rural environments usually have very low corrosion rates (<1 mpy).
- k) Bird droppings can also cause accelerated corrosion and unsightly stains.

3.8.4 Affected Units or Equipment

- a) Unpainted, uninsulated carbon steel and low-alloy steel piping and equipment operating below 250 °F (120 °C) where moisture can contact the surface.
- b) Uninsulated carbon and low-alloy steel equipment with deteriorated paint/coating.
- c) Equipment downwind of cooling towers and wet gas scrubbers.
- d) Equipment may be susceptible if cycled between ambient and higher or lower operating temperatures.
- e) Equipment shut down or idled for prolonged periods unless properly mothballed.
- f) Tanks and piping are particularly susceptible. Piping that rests on pipe supports is very prone to attack due to water entrapment between the pipe and the support.
- g) Piers and docks are very prone to attack from the marine environment.

- h) Bimetallic connections such as copper to aluminum electrical connections.

3.8.5 Appearance or Morphology of Damage

- a) The attack will be general or localized, depending upon the condition of the coating, if any, and whether or not the moisture is trapped.
- b) If there is no coating, corrosion or loss in thickness can be more general and widespread.
- c) Localized coating failures will promote localized corrosion.
- d) Metal loss may not be visually evident, although normally a distinctive iron oxide (red rust) scale forms as shown in [Figure 3-8-1](#).

3.8.6 Prevention/Mitigation

Paints or coatings are normally applied to otherwise unprotected equipment to prevent atmospheric corrosion. Surface preparation and proper coating application are critical for long-term protection in corrosive environments.

3.8.7 Inspection and Monitoring

- a) VT includes direct/line-of-sight and indirect methods using a camera, mirror, laser scanning, and/or structured white light imaging with pit gages.
- b) UT can include techniques like straight beam or angle beam (SWUT or PAUT) to directly measure remaining wall thickness or screening techniques using EMAT or GWT.
- c) RT may include traditional (film based), digital, or computed radiography media and may incorporate techniques such as contact or profile RT as well as open system imaging.
- d) ECT may include a screening technique such as pulsed eddy current (PEC).

3.8.8 Related Mechanisms

Corrosion under insulation (CUI) ([3.22](#)) and concentration cell (touch point) corrosion ([3.19](#)).

3.8.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.



Figure 3-8-1—Atmospheric corrosion of an LPG line in close proximity to a cooling tower.

3.9 Boiler Water and Steam Condensate Corrosion

3.9.1 Description of Damage

General corrosion and pitting in the boiler system and condensate return system. It is primarily the result of dissolved oxygen and/or carbon dioxide, which could lead to oxygen pitting corrosion and carbonic acid corrosion, respectively. Flow accelerated corrosion (FAC) in these systems may occur either as general wall thinning corrosion or localized corrosion at high velocity, high turbulence, or change of flow direction locations.

3.9.2 Affected Materials

Carbon steel and low-alloy steels.

3.9.3 Critical Factors

- Critical factors are the concentration of dissolved gas (oxygen and/or carbon dioxide), pH, temperature, quality of the feedwater, and the specific feedwater treating system.
- Corrosion protection in the boiler is accomplished by laying down and continuously maintaining a layer of protective Fe_3O_4 (magnetite).
- In the case of FAC, this protective oxide layer is dissolved or prevented from forming. Carbon steel is the most affected. Alloying elements in low-alloy steels such as Cr, Cu, and Mo can enhance corrosion resistance. The most critical temperature for FAC is 300 °F (150 °C), and it decreases with increasing pH. Too low an oxygen concentration increases the corrosion due to the inability to form the protective oxide layer. At least 3 ppb to 7 ppb may be required to form the oxide layer.
- The chemical treatment for scale and deposit control must be adjusted to coordinate with the oxygen scavenger for the specific water service and BFW treating system.
- Oxygen pitting can occur if the deaeration and oxygen scavenging treatment are not working correctly.

3.9.4 Affected Units or Equipment

- Corrosion can occur throughout the boiler water treatment system, including the deaerating equipment, feedwater lines, and pumps, as well as in the steam generation system including stage heaters, economizers, and boiler tubes as well as process unit steam generators.
- Corrosion in the condensate return system as well as in process unit reboilers and associated piping may be due to carbon dioxide, although oxygen pitting from oxygen contamination is also possible as well as FAC if the proper conditions are present.
- Threaded connections are especially susceptible.

3.9.5 Appearance or Morphology of Damage

- Corrosion from oxygen is normally a pitting type damage. It can occur anywhere in the system there is in-leakage of air or even if only very small quantities break through the oxygen scavenging treatment. Oxygen is particularly aggressive in equipment such as closed heaters and economizers where there is a rapid water temperature rise. (Figure 3-9-1)
- Carbon dioxide corrosion is normally smooth, but it can also cause grooving of the pipe wall. (Figure 3-9-2)
- Corrosion may be localized at areas where gases in the water are most concentrated, such as at the water to vapor interface level in a vertical reboiler.
- FAC failures are often located in areas where there is a flow disturbance such as an orifice run, flow meter, elbow, reducer, or other types of fittings. The wall thinning occurs just downstream of these flow disturbances.

leaving behind a corroded surface free of oxide scale, sometimes with a specific flow pattern. FAC has led to rupture of piping.

3.9.6 Prevention/Mitigation

- a) Oxygen removal from BFW typically includes mechanical deaeration followed by scavenging with catalyzed sodium sulfite or hydrazine, depending on the system pressure level. Proper deaerator operation and accurately controlled scavenger chemical addition are important. A residual of the oxygen scavenger is carried into the steam generation system to handle any oxygen ingress beyond the deaerator.
- b) If the scale and deposit control along with the magnetite maintenance treatment scheme do not minimize carbon dioxide corrosion in the condensate return system, an amine inhibitor treatment might be required.
- c) Boiler water needs to be blown down to control the concentration of solids and non-condensable gases. Steam equipment should be checked to ensure there are working non-condensable vents. It is also important that steam piping and equipment allow for blowdown of condensation (e.g. using steam traps and functional mechanical steam separation devices like coalescers).
- d) Water treatment, sampling, and analysis are the common methods used to ensure integrity and prevent boiler water and condensate corrosion.
 - 1. It may be necessary to modify or improve the water treatment program if problems such as a ruptured boiler tube or condensate leaks occur in the boiler water or condensate systems.
- e) The pH, temperature, and oxygen concentration are the main parameters that can affect the potential for FAC. BFW pH from 9.2 to 9.6 is often recommended. Upgrading the material to Cr-Mo steel usually solves the problem.
 - 1. Too low or total absence of oxygen is no longer considered the best corrosion control for BFW and condensate. Oxygenated treatments that deliberately inject oxygen into the condensate and BFW system or the use of oxygen scavenger at reduced concentrations may be necessary to maintain oxygen levels within the desired range to mitigate FAC.

3.9.7 Inspection and Monitoring

- a) Monitoring the appropriate parameters can indicate whether the treatment program is performing satisfactorily.
 - 1. Parameters that can be monitored through analysis include pH, alkalinity, hardness, conductivity, chlorine or residual biocide, dissolved gases (oxygen and carbon dioxide), iron, copper, and total dissolved solids
- b) Vacuum testing can be used to check for air ingress into the condenser hotwell.
- c) UT and RT methods can be used to monitor for pipe wall thinning.
- d) For boilers, there are no practical online inspection methods.
 - 1. UT and RT can be performed on boiler tubes and other boiler components when the system is offline.

3.9.8 Related Mechanisms

CO₂ corrosion (3.18), corrosion fatigue (3.21), erosion/erosion-corrosion (3.27), oxygenated water corrosion (3.49), and ammonia SCC of copper alloys (3.4).

3.9.9 References

- 1. *Betz Handbook of Industrial Water Conditioning*, Eighth Edition, Betz Laboratories, Trevose, PA, 1980.